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VERTICAL EDDY DIFFUSION AS A KEY MECHANISM FOR REMOVING PERFLUOROOCTANOIC ACID (PFOA) FROM THE GLOBAL SURFACE OCEANS

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Abstract

Here we estimate the importance of vertical eddy diffusion in removing perfluorooctanoic acid (PFOA) from the surface Ocean and assess its importance as a global sink. Measured water column profiles of PFOA were reproduced by assuming that vertical eddy diffusion in a 3-layer ocean model is the sole cause for the transport of PFOA to depth waters. The global oceanic sink due to eddy diffusion for PFOA is high, with accumulated removal fluxes over the last 40 years of 664 t, with the Atlantic Ocean accounting for 70% of the global oceanic sink. The global oceans have removed 13% of all PFOA produced to a depth greater than 100 m via vertical eddy diffusion; an additional 4 % has been removed

via deep water formation. The top 100 m of the surface oceans store another 21% of all PFOA produced (~1100 t)**.**

Keywords: *PFOA, global sink, diffusion, oceans, organic pollutants*

Capsule: *Vertical eddy diffusion is an important removal process for hydrophilic organic pollutants such as PFOA from the surface ocean.*

1. Introduction

Perfluoralkyl carboxylic acids (PFCAs) have been used by industry since the 1960s, mostly as a processing aid in the manufacture of fluoropolymers, such as during conversion of tetrafluoroethylene into polytetrafluoroethylene (PTFE) (Prevedouros et al., 2006). In the oceans, perfluorooctanoic acid (PFOA) is the most frequently detected PFCA, and often detected at greatest concentrations (Yamashita et al., 2005; Yamashita et al., 2008). Per- and polyfluoroalkyl substances compounds are transported away from their production and use locations by a combination of transport with ocean currents (Armitage et al., 2006), atmospheric transport and oxidation of fluorotelomer alcohols (Ellis et al., 2003), and transport with sea-salt aerosols (McMurdo et al., 2008; Webster and Ellis, 2008). Perflourinated compounds have been detected in biota, including humans world-wide (Giesy and Kannan, 2002; Houde et al., 2006); PFOA and perfluorooctane sulfonate (PFOS) are the most commonly detected perfluorinated chemicals in the environment. PFOS (but not PFOA) has been included in the Stockholm

47 treaty on 'Persistent Organic Pollutants' (POPs) due to its persistence, bioaccumulation
48 potential and toxicity (UNEP, 2009).
49 In general, the terrestrial environment and potentially the shelf sediments are considered
50 the main reservoir of POPs (Jonsson et al., 2003; Meijer et al., 2003). Atmosphere and
51 oceans can become important sinks for certain groups of POPs, such as dioxins and
52 furans (Lohmann et al., 2006a). In previous work we have presented a framework to
53 estimate the oceanic sink of POPs associated with settling particles ('biological pump')
54 (Dachs et al., 2002) and deep water formation ('physical pump') (Lohmann et al., 2006b).
55 The biological pump removes POPs from the surface ocean through a series of
56 partitioning steps involving dry and wet deposition, phytoplankton uptake and removal
57 from the surface mixed layer by the organic carbon settling flux (Dachs et al., 1999;
58 Dachs et al., 2002; Jurado et al., 2004; Jurado et al., 2005; Galban-Malagon et al., 2012).
59 The physical pump is especially important in the North Atlantic (Norwegian and
60 Labrador Seas) and the Southern Ocean (Weddell and Ross Seas), where both dissolved
61 and particle-bound POPs are removed from the surface ocean through deep water
62 formation (Broecker, 1974). For hydrophobic POPs, the physical pump is less important
63 globally than the biological pump (Lohmann et al., 2006b), but it might be more
64 important for hydrophilic chemicals. The magnitude and mechanisms of the oceanic sink
65 are poorly constrained for ionic and amphiphilic organic compounds which do not sorb
66 strongly to sinking organic matter.
67 The objective of this work is to estimate - for the first time - the importance of vertical
68 (eddy) diffusion as a major removal process of persistent compounds from the surface
69 ocean. We focus on PFOA, which in seawater exists primarily as the anion (PFO^-), no

70 matter whether its exact pKa value is around 3.7 (Burns et al., 2008) or -0.5 (Goss, 2008).
71 The anion has a very low sorption coefficient, a negligible vapor pressure and does not
72 degrade (Barton et al., 2007). Thus, PFOA has recently been proposed as a novel
73 chemical tracer of ocean circulation (Yamashita et al., 2008). SF_6 has also been
74 extensively used as a passive tracer to quantify vertical eddy diffusion coefficients but,
75 because it is biologically available to flora and fauna, SF_6 displays a stronger seasonal
76 variability than PFOA. Due to its low reactivity and, relative to other POPs, reduced
77 affinity for organic carbon, PFOA should be an excellent tracer of past and current
78 emissions, and its transport to the deep ocean will be due to subduction of water masses
79 and vertical eddy diffusion solely.
80 As the ocean is generally vertically stratified, there are large concentration gradients with
81 depth, so turbulent vertical eddy diffusion becomes a key process in removing
82 compounds from the surface layer. In analogy with Fick's First Law, the vertical flux of
83 compounds in the water due to vertical eddy diffusion, $F_{eddy\text{-}diff}$ (ng m^{-2} s^{-1}), is:

84 $$F_{eddy-diff} = -E\frac{\partial C}{\partial z}, \qquad (1)$$

85 where E is the vertical eddy diffusion coefficient (m^2 s^{-1}), C is the concentration of PFOA
86 (ng m^{-3}) and z (m) is the vertical coordinate (positive upwards with z = 0 indicating the
87 ocean surface).
88 Vertical eddy diffusivities are highly variable both in time and space, ranging from 10^{-5} -
89 10^{0} m^2 s^{-1} in the upper mixed layer of the ocean to 10^{-7} to 10^{-3} m^2 s^{-1} in the open deep
90 ocean (Gregg, 1987; Jurado et al., 2012a; Jurado et al., 2012b). A common approach for
91 modelling purposes is to consider the stratified ocean as a three-layer water column with
92 constant values of E in each layer: the highest values of E in the surface mixed layer,

93 reduced E values for the seasonal thermocline, and slightly increased E values below the
94 seasonal thermocline (Woods and Onken, 1982; Huisman and Sommeijer, 2002).
95 In this study, we use such a three-layer vertical eddy diffusion turbulence model to study
96 the removal of PFOA from the upper ocean. We investigate whether eddy diffusivity
97 fluxes can explain the reported vertical profiles of PFOA. Then, best-fit values of E are
98 obtained by reviewing the measured vertical profiles of PFOA from the few reports
99 published. These literature derived E values are then used to obtain global vertical
100 turbulent eddy diffusive fluxes of PFOA.
101 Therefore, the objectives of this study are (i) explain observed vertical PFOA profiles in
102 the Japan Sea and Mid-Atlantic Bight (Yamashita et al., 2008) solely based on transport
103 through vertical eddy diffusion, (ii) derive the eddy diffusion flux of PFOA at 100 m
104 depth from measured global surface ocean concentrations of PFOA, (iii) estimate
105 historical cumulative eddy diffusion fluxes of PFOA for the different oceanic regions, and
106 (iv) compare the importance of deep water formation and vertical eddy diffusion in
107 removing PFOA from the surface water to the mesopelagic and deep ocean.
108
109 **2. Materials and Methods**
110 ***2.1. Vertical water column concentrations of PFOA***
111 PFOA concentrations for the top 3,000 m of the water column were taken from
112 Yamashita et al. (2008). To date, Yamashita et al. (2008) is the only study that has
113 reported vertical ocean profiles of perfluoroalkyl compounds. The depth profiles from the
114 Japan Sea (JS2) and Mid-Atlantic Bight (AO4) were chosen as no deep water formation
115 occurs at these locations and data are available at a sufficiently high vertical resolution to

compare to model results. In the Japan Sea, concentrations of PFOA decreased from 50 ng m^{-3} at the surface to < 10 ng m^{-3} at 3,000 m depth. In the Mid-Atlantic Bight, concentrations dropped from ≤ 150 ng m^{-3} at the surface to ≤ 50 ng m^{-3} at 3,000 m.

2.2. Model description

PFOA reaches oceanic surface waters by atmospheric inputs and oceanic circulation (Ellis et al., 2003; Armitage et al., 2006) and we presuppose that it moves to depth via vertical eddy diffusion only. The physical process of vertical eddy diffusion, i.e., vertical turbulent mixing, tends to dominate other processes in most of the open ocean, which is vertically stratified. Chemical processes for PFOA, such as microbial or photolytic degradation and sorption to sinking particles are neglected in this work, since PFOA is a persistent chemical with low hydrophobicity (Prevedouros et al., 2006; Taniyasu et al., 2013).

The combination of equation (1) with a mass balance approach leads to Fick's Second Law, which models the change in time and space of the concentration field C(z,t):

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial z} F_{\text{eddy-diff}} = \frac{\partial}{\partial z}\left(E \left(\frac{\partial C}{\partial z} \right) \right), \qquad (2)$$

where z is the depth and t accounts for time. To solve equation (2), we partition the domain in space using water layers ranging from k=0 to k=N, where k=0 is the bottom layer at 3,000 m depth and k=N is the surface layer at 0 m depth, and with a uniform vertical depth increase of Δz = 1 m. We also partition the domain in time using time steps ranging from n=1 to n=M, where n=1 is the initial time at 1970 and n=M is the final time, and with a uniform time step increase of Δt = 0.5 years.

As initial conditions, we assume that at the initial time step (i.e., 1970) the seawater concentration of PFOA was zero (C = 0) at the surface and any depth. As boundary conditions, we assume that contaminants enter the water column from the ocean surface and we assume no flux of contaminants at the bottom of the domain:

$$C\big|_{z=0} = C_S \qquad (3a)$$

$$\left.\frac{\partial C}{\partial z}\right|_{z=-H} = 0 \qquad (3b)$$

where C_S are the measured water surface PFOA concentration, scaled on the predicted concentration trend for European seawater by van Zelm et al. (2008) (see below), and H is the depth of the bottom of the domain, i.e. 3,000 m.

To solve (2) with (3), we use an implicit method for discretization, the Crank-Nicholson method, which uses a backward difference at time, and it is based on the central difference in space and the trapezoidal rule in time:

$$\frac{C_k^{n+1} - C_k^n}{\Delta t} = \frac{1}{2}\frac{1}{\Delta z}\left(E_{k+1}\frac{C_{k+1} - C_k}{\Delta z} - E_{k-1}\frac{C_k - C_{k-1}}{\Delta z}\right)^{n+1} + \frac{1}{2}\frac{1}{\Delta z}\left(E_{k+1}\frac{C_{k+1} - C_k}{\Delta z} - E_{k-1}\frac{C_k - C_{k-1}}{\Delta z}\right)^{n} \qquad (4)$$

where k indicates the water layer, and n indicates the time step. E_{k+1} represents the vertical eddy diffusion coefficient at the mid-depth of the water layer above k, and E_{k-1} represents the vertical eddy diffusion coefficient at the mid-depth of the water layer below k.

This integration method is stable over the transition zones between the three layers, but this estimates the concentration field but not the eddy diffusivity fluxes. The vertical net eddy diffusion flux of compounds at a certain water layer k and a time step n, $F^{n}_{\text{eddy-diff, k}}$ (ng m^{-2} s^{-1}) is computed as:

159 $$-F^{n}_{eddy-diff,k} = -F^{n}_{eddy-diff,k-1} + \frac{C^{n+1}_{k} - C^{n}_{k}}{\Delta t}\Delta z \quad (5)$$

160

161 where $F_{eddy\text{-}diff,\ k\text{-}1}$ is the net flux of compounds at the layer below k due to vertical eddy
162 diffusion. The cumulative eddy diffusion flux since 1970 (i=0) to 2009 (i=n), at a certain
163 depth k, is given by, $F^{n}_{cum,\ k}$:

164 $$F^{n}_{cum,k} = \sum_{i=0}^{i=n} F^{i}_{eddy-diff,k} \quad (6)$$

165

166 The model used to estimate the transport by eddy diffusion holds the mass balance at each
167 depth (from equation [5]). In addition, we calculated the cumulative flux at 100 m depth,
168 which is the amount of PFOA leaving the top 100 m water layer from 1970 to 2009, and
169 compared it to the reservoir of PFOA at waters below 100 m depth for the last time period
170 considered (2009), and mass balance was achieved.

171

172 ***2.4. Forcing of the historical surface water concentration***

173 The industrial production of PFOA started around 1950 but initially the production
174 volume was small, so we assumed that significant loading to the ocean started in 1970
175 (Paul et al., 2009). Therefore, the surface water (representing the surface mixed layer)
176 concentration was forced to follow published trends starting in 1970. In 1970, the water
177 below the surface (i.e., below the mixed layer depth) was assumed to contain no PFOA.
178 For PFOA, surface water concentrations were scaled on the predicted concentration trend
179 for European seawater by van Zelm et al. (2008), with a zero concentration in 1970 and

180 then a linear increase from 1975 to 2009. We hence used the historical trend to estimate
181 past surface water concentrations. This approach assumes a direct link between emission
182 and resulting environmental concentrations, which has been observed for many other
183 POPs (Schwarzenbach et al., 2003).
184
185 ***2.5. Global ocean surface water concentrations of PFOA***
186 For the Atlantic Ocean, PFOA surface concentrations reported by Benskin et al. (2012)
187 and ranging from 3 ng m^{-3} (½ of detection limit) to 260 ng m^{-3}, have provided the best
188 spatial coverage to date. There are fewer reported PFOA concentrations for the Pacific
189 and Indian Ocean. In the Pacific Ocean, concentrations range from below detection limit
190 to 50 ng m^{-3} (Wei et al., 2007; Yamashita et al., 2008); we used a range of 5 – 50 ng m^{-3}.
191 In the Indian Ocean, reported concentrations are up to 10 ng m^{-3} (Wei et al., 2007); we
192 assumed a range of 1 – 10 ng m^{-3}. We defined the southern boundary for these ocean
193 basins as the southernmost latitude where PFOA was still consistently reported above the
194 detection limit.
195
196 **2.6. E values and extent of each water layer for the global oceans**
197 Values of the vertical eddy diffusion coefficient, E, are scarce in the open ocean. We
198 represent the variation of E with depth as a three-layer structure, with a constant but
199 different E value in each water layer. The lower boundary of the first layer ($z = -H_1$) is
200 taken as the diurnal mean mixed layer depth; the second layer (with lower boundary $z = -H_2$) goes from the base of the diurnal mean mixed layer depth to the base of the seasonal
202 thermocline; the third layer goes from the base of the seasonal thermocline to the bottom

of the studied domain ($z = - H_3 = -3{,}000$ m). Furthermore, at the boundary of each water layers, we assume a gradual change of E, with a constant gradient within 20 m at each side of the boundary (or within 5 m if the water layer is very shallow).

To compute global ocean vertical eddy diffusion fluxes, we use E values from various microprofiler survey campaigns in the Atlantic and Pacific Oceans (Gregg, 1987; Ruddick et al., 1997; Jurado et al., 2012a; Jurado et al., 2012b) and common reported H values in the global oceans. For the diurnal mean mixed layer, we use an average E_1 of 10^{-2} m^2 s^{-1}, ranging from 10^{-5} to 10^{0} m^2 s^{-1}, and an average depth of H_1=60. For the seasonal thermocline, we use an average E_2 of 10^{-5} m^2 s^{-1}, ranging from 10^{-7} to 10^{-3} m^2 s^{-1}, and an average depth H_2=600 m. Below the seasonal thermocline, we used an average E_3 of 10^{-4} m^2 s^{-1}, ranging from 10^{-6} to 5 x 10^{-3} m^2 s^{-1}, and H_3=3,000 m. Note the large variability of the vertical eddy diffusion coefficients values, which can be up to 5 orders of magnitude, but this variability is usually observed when measuring turbulence with microprofilers (Jurado et al., 2012a; Jurado et al., 2012b). H_1 and H_2 are also subject to seasonal and spatial changes, which are not considered here.

3. Results and Discussion

3.1. Model results and comparison with measured distribution

First, we aimed to reproduce the measured PFOA profile (Yamashita et al., 2008) for the top 3,000 m of the Japan Sea (Figure 1a). Using three values for the vertical eddy diffusion coefficient E (E_1 = 5 x10^{-3} m^2 s^{-1} in the mixed layer [-10 m, 0 m] , E_2 = 8 x 10^{-4} m^2 s^{-1} in the seasonal thermocline [-300 m, -10 m], and E_3 = 2.5 x10^{-3} m^2 s^{-1} below the base of the seasonal thermocline [-3,000 m, -300 m]), constant in time and with a gradual

227 change within layers, results in an excellent agreement between modeled and measured
228 PFOA concentrations (Yamashita et al., 2008) for profile JS2 in the Japan Sea (Figure
229 1a). The depth of the surface mixed layer ($z = - H_1 = -10$ m) and the depth base of the
230 seasonal thermocline ($z = - H_2 = -300$ m) are consistent with measured temperature and
231 salinity profiles in Yamashita et al. (2008). Measured PFOA concentrations at all depths
232 were within a factor of 2 for the Japan Sea, or less (upper water column) of the model
233 predictions. In general, our simple vertical eddy diffusion model can reproduce the
234 observed profile for PFOA for the top of the water column extremely well, suggesting
235 that vertical eddy diffusion has been solely responsible for the transport of PFOA to
236 deeper waters. However, the E values needed to fit the field measurements of PFOA are
237 close to the upper range of the E values measured in the field, and such efficient transport
238 of PFOAs to deep waters may not be a generalized process in all the oceans.
239 While Yamashita et al. (2008) have measured other vertical profiles, PFOA was not
240 detected in their South Pacific Ocean samples. The vertical profiles reported in the North
241 Atlantic Ocean were taken in the region of deep water formation and hence the model
242 here cannot be applied. Lastly, their profiles for the Mid-Atlantic Ocean display an
243 unusually deep seasonal thermocline, but one of these profiles (AO4) appears consistent
244 with transport solely due to vertical eddy diffusion. In this case, the mixed layer depth is
245 around 100 m, and the base of the seasonal thermocline at 800 m, resulting in higher E
246 values ($E_1 = 5 \times 10^{-3}$ m^2 s^{-1} (0-100 m), $E_2 = 3.5 \times 10^{-3}$ m^2 s^{-1} (100-800 m) and $E_3 = 4 \times 10^{-3}$
247 m^2 s^{-1} (800-3,000 m) for the cast AO4 (see Figure 1b). Model predictions were within
248 20% of the measured values.

Our derived E values are at the upper end of the E reported elsewhere, which can vary by more than 5 orders of magnitude. The large E values may be affected by the particular conditions of the sampling sites, such as additional horizontal advection driving turbulence transport of these compounds by deeper currents. Further vertical profiles of PFOA are needed to verify its potential as a diffusion tracer, but to date only Yamashita et al.[17] provided depth profiles. The vertical dependence of E, with large values in the surface layer, depleted values in the seasonal thermocline and somewhat increased values below the seasonal thermocline, is in agreement with the E distribution reported elsewhere (Gregg, 1987; Ruddick et al., 1997; Jurado et al., 2012a). We conclude that the assumption that PFOA move to depth solely via vertical turbulent diffusion is consistent with available observations.

3.2. The removal flux of PFOA at 100 m depth across the global oceans

We estimated fluxes of PFOA due to vertical diffusion at 100 m depth across the major ocean basins using equation (5) with the set of E values and depths of the bottom of the diurnal mean mixed layer and seasonal thermoclines determined for the global oceans. In the Atlantic Ocean, vertical diffusive fluxes of PFOA were based on PFOA concentrations in surface waters measured in 2007 and 2009 by Benskin et al. (2012), scaled back to zero in 1970 based on the trend reported by van Zelm et al. (2008). For the Pacific Ocean, we used the range of concentrations reported in Yamashita et al. (2008) and Wei et al. (2007). For the Indian Ocean, we used the range of concentrations reported in Wei et al. (2007).

271 Figures 2 and 3 show the change in time and depth of the modeled PFOA concentration
272 and fluxes. The concentrations in surface waters increase from 1970 to 2009, with a
273 continuous decrease in concentrations and fluxes with depth. Right panels in figure 2
274 show the 2009 profiles using the average, lower limit and upper limit E values. We chose
275 station 25 in the 2009 *Endeavor* Cruise in Benskin et al. (2012) as a typical example of
276 open ocean measurements in the North Atlantic. The derived historical profiles of the
277 concentration and vertical eddy diffusive flux for PFOA over the last four decades,
278 assuming increasing surface concentrations, are displayed in Figure 3. Due to vertical
279 eddy diffusion, PFOA concentrations in the water column increase, and PFOA reaches
280 deeper waters due to eddy diffusivity.
281 We estimated whether volatilization of PFOA could be another important loss process of
282 PFOA from surface waters relative to vertical diffusion. Even assuming its pKa = 3.7
283 (Burns et al. 2008), the concentrations of the non-ionic (acid) form of PFOA will be very
284 low, and estimations of gross volatilization fluxes using the standard two-film models for
285 diffusive air-water exchange points out that it would be at most 10% of its transfer to
286 depth due to eddy diffusivity. Assuming a pKa=-0.5 (Goss et al. 2008), these
287 volatilization fluxes are more than five orders of magnitude lower than eddy diffusivity
288 fluxes. Thus, we consider PFOA to be a persistent, water-borne tracer that will only be
289 removed from surface waters to depth.
290 The historical cumulative flux at 100 m depth from 1975 to 2007 were highest (-
291 $15x10^3$ to -8,6 $x10^3$ ng m^{-2}) in the North Atlantic. Fluxes decreased towards -3,8 $x10^3$ to -
292 2,4 $x10^3$ -ng m^{-2} near the Equator, and were even lower in the South Atlantic (Table 1).

293 The lowest cumulative PFOA fluxes were estimated for the Pacific and Indian Ocean, -
294 1,6 x10^3 ng m^{-2} and -310 ng m^{-2}, respectively.
295
296 **3.3. Comparison between removal fluxes of PFOA from the global Oceans due to**
297 **vertical eddy diffusion and deep water formation**
298 Previous results highlight that East-West gradients of PFOA in surface waters of the
299 North Atlantic are rather small. For example, PFOA varies by less than a factor of two on
300 a transect between 45^0N and 60^0N (Yamashita et al., 2008). Similarly, the Yamashita et
301 al. (2008) transect at 15^0N showed little variability in PFOA, except for one elevated
302 sample, which was probably influenced by the Amazon River plume. This suggests that
303 atmospheric deposition fluxes were either fairly constant longitudinally across the
304 Atlantic and/or presumably accounted for a small fraction of the overall inputs of PFOA
305 in most oceanic regions, as was reported for the Arctic Ocean (Armitage et al., 2009b;
306 Stemmler and Lammel, 2010); the major uncertainty would remain with the vertical eddy
307 diffusion coefficients. We therefore estimated the importance of the global Oceans in
308 removing PFOA from the surface Ocean due to vertical diffusion by extrapolating our
309 flux estimates across a given region (Table 1 and 2).
310 Due to the high variability in reported E values, using the upper and lower limit of the
311 used E values resulted in estimations of eddy diffusivity fluxes that also varied by several
312 orders of magnitude (Table 1). While the instantaneous turbulent fluxes may be highly
313 variable, it is unlikely that a certain region constantly displays values of E close to the
314 upper limit or lower limit. Therefore, the predictions obtained using the average E values
315 seem appropriate to evaluate the mid- long-term fate of PFOA, even though the upper and

316 lower limits provide extreme estimates of the range of the potential importance of this
317 mechanism of transport (Tables 1 and 2).
318 The North Atlantic emerged as the main sink for PFOA, with cumulative removal fluxes
319 below 100 m depth over the last 40 years of ca. 470 t, with the South Atlantic
320 contributing another ~ 74 t. The Pacific Ocean is estimated to have around 190 t PFOA
321 below a depth of 100 m, while the Indian Ocean contributed only 11 t in total. The global
322 oceanic sink of PFOAs due to eddy diffusivity is in the order of 660 t (Table 2).
323 To put the vertical diffusive flux values in the global oceans in perspective, we estimated
324 the flux of PFOA entering the deep Ocean via deep water formation. Deep water
325 formation fluxes were as in (Lohmann et al., 2006b), with the Norwegian and Labrador
326 Sea having areas of 4.0 and 2.7×10^{12} m^2, and average deep water formation fluxes of 10
327 and 5 Sv (10^6 m^3 s^{-1}). PFOA surface water concentrations of 20 - 50 ng m^{-3} were
328 measured in the Labrador Sea water column by Yamashita et al. (2008), while Ahrens et
329 al. (2010) reported 10 ng m^{-3} for the Norwegian Sea. We note that for a given region in
330 the Atlantic Ocean, PFOA concentrations by Yamashita et al. (2008) seem higher by a
331 factor of around 2 than those reported by Ahrens et al. (2009). A similar discrepancy was
332 obtained for PFOA concentrations in seawater in a recent inter-laboratory comparison
333 between Japan's National Institute of Advanced Industrial Science and Technology (
334 factor of 2 higher) and the Canadian Centre for Inland Waters (Environment Canada),
335 implying a systematic error, most likely by the Japanese group (Benskin et al., 2012).
336 Estimated fluxes of PFOA are 3 - 16 and 2 - 8 tons yr^{-1} in the Norwegian and Labrador
337 Sea for surface concentrations of 10 - 50 ng m^{-3}. PFOA was not detected in the other two
338 deep water formation regions, the Ross and Weddell Seas (Yamashita et al., 2008). The

maximum contribution of these Southern Seas in transporting PFOA to deep water can be estimated by assuming ½ detection limit by Yamashita et al. (2008) (of 6 ng m^{-3}) as PFOA concentrations. This would give rather insignificant fluxes of at most 1 ton yr^{-1} for each Sea. The deep water formation fluxes are similar in importance to the estimated inflow of PFOA into the Arctic Sea of 2-12 t yr^{-1} (Prevedouros et al., 2006) or 8-23 t yr^{-1} (Stemmler and Lammel, 2010). Assuming that the increase of PFOA in the North Atlantic mirrored the PFOA emissions, we can extrapolate the total amount of PFOA moved to deep waters since their industrial production started in 1970. Total amounts moved by deep water formation are estimated to be 50 - 250 tons in the Norwegian Sea and 30 - 130 tons of PFOA in the Labrador Sea over the last 40 years. Thus, vertical eddy diffusion accounts for losses of PFOA to depth on the order of 660 t (range from 1 to 4800 t), while 80 – 360 tons have been lost from the surface oceans via deep water formation.

Based on measured surface concentrations, we extrapolated the amount of PFOA residing in the top 100 m of the water column (Table 2). At most, there is a 10% decline of surface water concentrations to 100 m depth, no matter which E values we chose. This equates to approximately another 1100 tons PFOA stored in the upper 100m of the world's Oceans: mostly in the North Atlantic and Pacific Ocean (around 600 and 300 t respectively), another 170 t in the South Atlantic), and 19 t in the Indian Ocean.

Prevedouros et al. (2006) reported a total historical industrial production of PFOA of 3,200 – 7,300 tons. Here we assume the average of the reported range (i.e., 5,250 tons) as the most likely production volume. Our results imply that the global Oceans have removed around 13% of the PFOA produced to depth greater than 100 m via vertical diffusion, but with a large range due to uncertainty of eddy diffusivity measurements

362 (range between 0.03 and 91% of global production). An additional 4% (1.5- 6.8%) will
363 have been removed via deep water formation. Lastly, the top 100 m of the surface oceans
364 store another 21% of all PFOA produced (1120 t, Table 2).
365 As not all produced PFOA is expected to have escaped its intended use (Prevedouros et
366 al., 2006), our calculations suggest that the majority of PFOA has reached the deeper
367 ocean via vertical diffusion. To the best of our knowledge, this work suggests that vertical
368 diffusion to the deep ocean is the main known sink of PFOA from the environment, even
369 though this process has not been considered in current models of PFOA transport and fate
370 in regional and global models (Armitage et al., 2009a). We note that coastal oceans, such
371 as the Japan Sea, will likely exhibit markedly higher fluxes to depth, due to a combination
372 of more efficient vertical mixing and greater surface concentrations of PFOA.
373

374 **4. Implications**

375 Our results suggest that a simple eddy-diffusion model can explain the vertical profile of
376 persistent organic compounds, that are neither prone to air-water exchange nor to
377 degradation reactions, such as PFOA, in the surface ocean. We show here that vertical
378 eddy diffusion fluxes are significantly higher than those due to deep water formation, thus
379 being the main environmental known sink for PFOA. Over time, it seems likely that
380 perfluorinated compounds will accumulate in larger concentrations in the open ocean,
381 increasing the role of vertical eddy diffusion as a sink process even more.
382 Curiously, transport due to vertical eddy diffusion has never been considered before as a
383 significant sink of POPs, probably due to the fact that most POPs are hydrophobic and
384 their settling associated to organic carbon is faster. In any case, vertical diffusion is a

slow but persistent and ubiquitous sink that could also be important for other POPs, and it will be the main sink for the "swimmer" type of pollutants.

Once emissions are abated, surface concentrations will decrease fast initially, but will slow down as eddy diffusion reduces the concentration gradient in the water column. Our results could also explain observations noticing a very slow response of global oceans with respect to decreasing concentrations of other POPs. It seems likely that after an initial fast decline as a response to decreasing inputs, ocean surface waters could enter a phase during which concentrations decrease only slowly, making these difficult to detect with the current analytical precision. For "swimmer" type compounds, such as PFOA, this lack of clear temporal trends will be due to the fact that vertical diffusion is the main sink process. For single-hoppers and multiple-hoppers, such as legacy POPs, in the large oligotrophic areas of the oceans, the biological pump is not an efficient removal process (Jurado and Dachs, 2008). It is possible that vertical diffusion has been the main sink, and nowadays, after a reduction of atmospheric inputs, the concentration gradients have decreased, or inverted, such that there is an upper direction flux of legacy POPs so the oceans are acting as a source to the atmosphere (Nizzetto et al., 2010; Zhang and Lohmann, 2010; Lohmann et al., 2012) .

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Table 1: Ocean regions, selected range of PFOA concentrations, average of calculated turbulent fluxes at 100 m depth ($F_{ave, 100}$) and the historically cumulative turbulent fluxes (1970-2009) at 100 m depth ($F_{cum, 100}$). Computations made with average and range E values reported for the global oceans.

		Average E values for the global oceans ($E_1=10^{-2}$, $E_2=10^{-5}$, $E_3=10^{-4}$ m^{-2} s^{-1})		Upper range E values for the global oceans ($E_1=10^{-1}$, $E_2=10^{-3}$, $E_3=5*10^{-3}$ m^{-2} s^{-1})		Lower range E values for the global oceans ($E_1=10^{-5}$, $E_2=10^{-7}$, $E_3=10^{-6}$ m^{-2} s^{-1})	
	[PFOA]						
Ocean region	(pg/L)	$F_{ave, 100}$ [ng m^{-2} s^{-1}]	$F_{cum, 100}$ [ng m^{-2}]	$F_{ave, 100}$ [ng m^{-2} s^{-1}]	$F_{cum, 100}$ [ng m^{-2}]	$F_{ave, 100}$ [ng m^{-2} s^{-1}]	$F_{cum, 100}$ [ng m^{-2}]
N-Atlantic, (45-60 °N	260[a]	-2.4*10^{-5}	-1.5*10^{4}	-1.6*10^{-4}	-11*10^{4}	-1.4*10-7	-34
N-Atlantic, (30-45 °N)	21-250[a]	-2.1*10^{-5}	-1.4*10^{4}	-1.4*10^{-4}	-10*10^{4}	-1.3*10^{-7}	-31
N-Atlantic, (15-30 °N)	24-210[a]	-1.3*10^{-5}	-8,600	-8.6*10^{-5}	-6.3*10^{4}	-7.8*10^{-8}	-19
N-Atlantic, (0-15 °N)	18-41[a]	-5.2*10^{-6}	-3,800	-3.4*10^{-5}	-2.7*10^{4}	-3.1*10^{-8}	-8
S-Atlantic (0-15 °S)	10-32[a]	-3.9*10^{-6}	-2,400	-2.5*10^{-5}	-1.7*10^{4}	-2.3*10^{-8}	-5
S-Atlantic (15-30 °S)	5-27[a]	-3.1*10^{-6}	-2,000	-2.0*10^{-5}	-1.5*10^{4}	-1.9*10^{-8}	-5
S-Atlantic (30-45 °S)	3-110[a]	-4.3*10^{-6}	-2,800	-2.8*10^{-5}	-2.0*10^{4}	-2.5*10^{-8}	-6
S-Atlantic (45-60 °S)	5-8[a]	-5.6*10^{-7}	-360	-3.6*10^{-6}	-2,600	-3.2*10^{-9}	-1
Pacific (30 °S–60 °N)	5-50[b,c]	-2.4*10^{-6}	-1,600	-1.6*10^{-5}	-1.1*10^{4}	-1.4*10^{-8}	-3
Indian (30 °S–30 °N)	1-10[c]	-4.8*10^{-7}	-310	-3.1*10^{-5}	-2,300	-2.8*10^{-9}	-1

[a] (Benskin et al., 2012); [b] (Yamashita et al., 2008); [c] (Wei et al., 2007)

Table 2: Ocean basins, their surface areas, calculated amount of PFOA removed from the top 100 m due to turbulence ($F_{cum, 100}$ * surface area, from 1970-2009) versus PFOA fluxes due to deep water formation and amount of PFOA stored in the top 100 m surface oceans

Ocean basins	Surface area (10^6 km^2)	Amount PFOA removed by turbulence from top 100 m (tons)			deep water formation (tons)	Amount of PFOA top 100 m (tons)
		average E values	lower range E values	upper range E values		
Norwegian Sea	4.0	n/a	n/a	n/a	50-250	
Labrador Sea	2.7	n/a	n/a	n/a	30-130	
N-Atlantic, 45 N – 60 N	8	124	0.3	904	n/a	205 (153 - 209)
N-Atlantic, 30 N – 45 N	10	139	0.3	1006	n/a	232 (174 - 237)
N-Atlantic, 15 N – 30 N	11	95	0.2	690	n/a	159 (119 - 162)
N-Atlantic, 0 N - 15 N	9	34	0.1	247	n/a	51 (39 - 52)
S-Atlantic, 0 N - 15 S	9	21	0.0	154	n/a	39 (29 - 39)
S-Atlantic, 15 S - 30 S	11	22	0.0	163	n/a	39 (29 - 39)
S-Atlantic, 30 S - 45 S	10	28	0.1	202	n/a	46 (34 - 47)
S-Atlantic, 45 S - 60 S	8	3	0.0	21	n/a	5 (4 -5)
Pacific, 30 S - 60 N	120	186	0.4	1352	n/a	326 (245 - 332)
Indian, 30 S – 30 N	35	11	0.0	79	n/a	19 (14 - 19)
Total (range)		**664**	**1.5**	**4818**	**220** (80 – 360)	**1120** **(839 - 1142)**

Figure captions

Figure 1: Modeled versus measured concentration of PFOA in (a) the Japan Sea (cast JS2, May 2005 Yamashita et al. [2008]) using E_1=5 x10^{-3} m^2 s^{-1} [0 , -10 m], E_2=8 x10^{-4} m^2 s^{-1} [-10 , -300 m], and E_3=2.5 x10^{-3} m^2 s^{-1} [-300, -3,000 m], and (b) in the Mid-Atlantic Bight (cast A04, March 2004, Yamashita et al. [2008]) using E_1= 5 x10^{-3} m^2 s^{-1} [0, 100 m], E_2= 3.5 x10^{-3} m^2 s^{-1} [-100, -800 m], and E_3= 4 x10^{-3} m^2 s^{-1} [-800, -3,000 m].

Figure 2: (a,b) Modeled concentration of PFOA and (c,d) modeled removal flux of PFOA due to vertical eddy diffusion in the station 25 in the *R/V Endeavor* Cruise at Benskin et al. [2012]. Panel (a) and (c) show modeled concentration and flux from 1970 until 2009, obtained from the average vertical eddy diffusivity, E, values for the global oceans: E_1 = 10^{-2} m^2 s^{-1} in the surface mixed layer (0-60 m), E_2 = 10^{-5} m^2 s^{-1} in the seasonal thermocline (60-600m), and E_3 = 10^{-4} m^2 s^{-1} below the seasonal thermocline (600-3,000m). Panel (b) and (d) show vertical profiles for the year 2009, using the average E values (solid line), upper range of the E values (dashed line): E_1 = 10^{0} m^2 s^{-1} , E_2 = 10^{-3} m^2 s^{-1}, E_3 = 5 x10^{-3} m^2 s^{-1} , and lower range of the E values (dotted line): E_1 = 10^{-5} m^2 s^{-1}, E_2 = 10^{-7} m^2 s^{-1}, E_3 = 10^{-6} m^2 s^{-1}.

Figure 3: Historical profiles (0 – 3,000 m) of (a) the modeled PFOA concentration, and (b) the modeled removal flux of PFOA due to vertical eddy diffusion in the station 25 in the 2009 *R/V Endeavor* cruise at Benskin et al. [2012]. Concentrations and fluxes are given for the years 1970 (just before PFOA large scale production), 1980, 1990, 2000 and 2009. Concentrations and fluxes have been predicted using representative vertical eddy diffusivity, E, values for the global oceans: E_1 = 10^{-2} m^2 s^{-1} in the surface mixed layer (0-60 m), E_2 = 10^{-5} m^2 s^{-1} in the seasonal thermocline (60 - 600 m), and E_3 = 10^{-4} m^2 s^{-1} (600 - 3,000 m).